

## Dielectric relaxation studies of ternary mixtures of non-rigid polar liquids in the MW region

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**Abstract** . The dielectric behaviour of three Acrylates and their mixture compositions as liquid dielectric samples, have been studied at MW frequency 9.132 GHz in dilute solution of carbon tetrachloride in the temperature range 300K to 330K. Different dielectric parameters like dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  at microwave frequency, static dielectric constant  $\epsilon_1$  and dielectric constant  $\epsilon_\infty$  at optical frequency have been determined. Using these dielectric data, various relaxation times viz  $\tau_0$ ,  $\tau_1$  and  $\tau_2$ , of individual components and their ternary mixture compositions have been calculated. The relaxation time values for single component solutions agree well with literature values while relaxation times of ternary mixture compositions are consistent with the computed values obtained from various theoretical relations.

**Keywords** : Dielectric constant, dielectric loss, dipole moment and relaxation time

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### 1. Introduction

Though many workers [1-4] have done extensive work on dielectric behaviour of dilute solutions of polar liquids and their binary mixtures in non-polar solvents, reported work on higher order systems is negligibly small. Very little information on the study of non-rigid polar mixtures in solutions is available even at a single temperature. The dielectric relaxation studies of ternary mixtures of polar liquids in dilute solutions of non-polar liquid provide valuable information about solute-solute and solute-solvent interactions. In order to provide experimental data on ternary mixture composition and to test existing theoretical relations, three Acrylates namely Butyl acrylate (BA), Butyl methacrylate (BMA), Iso-butyl methacrylate (IBMA) and their mixture compositions at four different temperatures are studied. The study is expected to provide better understanding of the nature of molecular orientation processes. Molecules of solutes under investigation are non-rigid and associative in nature. The dipole moment values of these acrylates are approximately same (1.97-2.10 D); therefore, it can be assumed that the internal fields of the mixtures will not be different from internal fields of the

pure components of the mixture. Moreover, it is expected that relaxation behavior of mixture must depend on the concentration of individual component and temperature of the mixture.

### 2. Experimental details and theory

The experimental set-up, procedure and principle involved in determining dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  at microwave frequency 9.132 GHz is the same as described earlier by Yadav and Gandhi [5,6]. The  $\epsilon'$  and  $\epsilon''$  of sample are obtained by using the following set of equations :

$$\epsilon' = \left( \frac{\lambda_0}{\lambda_c} \right)^2 + \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left[ 1 - \left( \frac{\alpha_d}{\beta_d} \right)^2 \right], \quad (1)$$

$$\epsilon'' = 2 \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left( \frac{\alpha_d}{\beta_d} \right). \quad (2)$$

Here,  $\lambda_0$ ,  $\lambda_c$  and  $\lambda_d$  are free space wavelength, cut-off wavelength and wavelength in the dielectric sample respectively.

$\alpha_d$  is attenuation constant of the material measured in nepers per meter and  $\beta_d$  is phase shift per unit length of the sample

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measured in radians per meter and are experimentally measured by following relations :

$$\alpha_d = \frac{2.302}{2L} \log \left| \frac{\sqrt{x_1}}{2\sqrt{x_2} - \sqrt{x_1}} \right| \quad (3)$$

$$\beta_d = \frac{2\pi}{\lambda_d} \quad (4)$$

Here,  $x_1$  and  $x_2$  are readings of power indicating meter without and with liquid sample of length  $L$  in dielectric cell.

Static dielectric constant  $\epsilon_s$  of samples are measured with the help of a Toshniwal RL-09 dipolemeter, which is based on heterodyne beat method. Dielectric constant of samples at optical frequency  $\epsilon_\infty$  are measured with Abbe's refractometer by squaring the refractive indices ( $n_D$ ) for sodium D-line. The compounds under investigation are of standard grade and used as such without further purification. All these measurements are taken at four temperatures 300K, 310K, 320K and 330K. Temperature of mixtures was kept constant within  $\pm 0.5$  K by using a constant temperature water bath. In eq. (1),  $\lambda_d$  is the only experimentally measurable quantity since for dilute solution of polar liquids in non-polar solvents,  $[1 - \alpha_d^2 / \beta_d^2] \approx 1$  as  $\alpha_d \ll \beta_d$ . Here  $\lambda_d$  is measured by means of plunger displacement inside the liquid filled in the dielectric cell. The precision of measurement for  $\lambda_d$  is  $\pm 0.001$  cm. Corresponding to this accuracy value, the error in the measurement of  $\epsilon'$  is estimated. For simplification, errors due to non-zero impedance of short circuit plunger, curvature of mica window separating E-plane band from dielectric cell and clamping gaps in wave-guide section are ignored. The errors of measurement are calculated by using conventional method of error analysis [7]. This method states that if a quantity  $Q$  depends on several observable quantities  $x, y, \dots$ , such that  $Q$  is a known function of variables,  $Q = f(x, y, \dots)$ , then error  $q$  of the quantity  $Q$  may be obtained from :

$$q = \left[ q_x^2 \left( \frac{\partial f}{\partial x} \right)^2 + q_y^2 \left( \frac{\partial f}{\partial y} \right)^2 \right]^{1/2} \quad (5)$$

Here,  $q_x, q_y, \dots$  are the errors of the measured values of  $x, y, \dots$ . This relation is valid even if the precision of the respective measurements differs [7]. The eq. (2) indicates the presence of  $\alpha_d, \beta_d$  and  $L$  terms in addition to  $\lambda_d$  in the expression of  $\epsilon''$ . The error involved in measurement of  $\epsilon''$  is also calculated by using eq. (5). Considering these calculations, errors involved in the measurement of  $\epsilon'$  and  $\epsilon''$  are approximately  $\pm 1\%$  and  $\pm 5\%$  respectively.

The values of distribution parameter  $\alpha$ , most probable relaxation time  $\tau_0$ , relaxation time  $\tau_1$  for molecular rotation and relaxation time  $\tau_2$  for intramolecular rotation are determined experimentally by using the well-established method of Higasi

*et al* [8]. The expressions used to compute distribution parameter  $\alpha$  and various relaxation times are :

$$\alpha = 1 - \frac{2}{\pi} \tan^{-1} \left[ \frac{(\epsilon_s - \epsilon_\infty)\epsilon''}{(\epsilon_s - \epsilon')(\epsilon_s - \epsilon_\infty) - (\epsilon'')^2} \right] \quad (6)$$

$$\tau_0 = \frac{1}{\omega} \sqrt{\frac{(\epsilon_s - \epsilon')}{(\epsilon' - \epsilon_\infty)}} \quad (7)$$

$$\tau_1 = \frac{1}{\omega} \left( \frac{\epsilon''}{(\epsilon' - \epsilon_\infty)} \right) \quad (8)$$

$$\tau_2 = \frac{1}{\omega} \left( \frac{(\epsilon_s - \epsilon_\infty)}{\epsilon''} \right) \quad (9)$$

Here,  $\omega$  is angular frequency of e.m. wave. These parameters involve  $\epsilon'$  and  $\epsilon''$  quantities in their expressions. Due to errors in  $\epsilon'$  and  $\epsilon''$ , the calculated errors in dielectric parameters  $\alpha, \tau_0, \tau_1$  and  $\tau_2$  are  $\pm 5\%, \pm 6\%, \pm 12\%$  and  $\pm 5\%$  respectively.

Static dielectric constant  $\epsilon_s$ , dielectric constant  $\epsilon_\infty$  at optical frequency, dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  at microwave frequency, distribution parameter  $\alpha$ , the most probable time  $\tau_0$ , relaxation times  $\tau_1$  and  $\tau_2$  for pure components and their ternary mixture compositions at four different temperatures are reported in Table 1.

The most probable time  $\tau_0$  for mixture compositions has been computed by three theoretical methods [9-11] viz.

Simple mixing rule (SM) :

$$(\tau_0)_{mix} = \sum_{i=1}^3 x_i \tau_i \quad (10)$$

Reciprocal mixing rule (RM) :

$$\left( \frac{1}{\tau_0} \right)_{mix} = \sum_{i=1}^3 \frac{x_i}{\tau_i} \quad (11)$$

Yadav and Gandhi method (Y & G) :

$$(\tau_0)_{mix} = \sqrt{\frac{\sum_{i=1}^3 x_i \tau_i^2}{\sum_{i=1}^3 x_i}} \quad (12)$$

Here,  $x_i = 1, 2, 3$  are mole fractions of individual components in the mixture composition.

Experimental values of most probable relaxation times  $(\tau_0)_{mix}$  of mixture compositions are compared with theoretical computed values by using above mentioned methods and are listed in Table 2.

Table 1. Dielectric parameters and relaxation times of pure acrylates and their ternary mixtures at different temperatures.

Sl. No.	Name of the sample	Temp.	$\alpha$	$\epsilon_s$	$\epsilon_\infty$	$\epsilon'$	$\epsilon''$	$\tau_0 \times 10^{12}$	$\tau_1 \times 10^{12}$	$\tau_2 \times 10^{12}$
1	Butyl acrylate (BA)	300 K	0.377	2.51	2.128	2.396	0.120	11.41	7.83	16.65
		310 K	0.365	2.49	2.102	2.384	0.119	10.77	7.41	15.66
		320 K	0.337	2.46	2.080	2.369	0.118	10.19	7.17	14.15
		330 K	0.401	2.45	2.061	2.358	0.118	9.70	6.92	13.59
2	Iso Butyl Methacrylate (IBMA)	300 K	0.333	2.53	2.127	2.438	0.123	9.37	6.92	12.70
		310 K	0.266	2.50	2.105	2.425	0.122	8.44	6.64	10.72
		320 K	0.263	2.47	2.095	2.406	0.121	7.75	6.78	8.87
		330 K	0.238	2.44	2.079	2.384	0.120	7.14	6.84	7.45
3	Butyl Methacrylate (BMA)	300 K	0.337	2.58	2.129	2.487	0.126	8.95	6.16	13.56
		310 K	0.322	2.55	2.108	2.474	0.125	7.95	5.95	10.60
		320 K	0.271	2.52	2.088	2.454	0.124	7.21	5.93	8.78
		330 K	0.215	2.49	2.071	2.441	0.123	6.45	5.79	7.18
4.	T. Mix. No. 1 (BA+IBMA+BMA) (.0696+.3035+.6269)*	300 K	0.344	2.56	2.128	2.464	0.124	9.32	6.44	13.49
		310 K	0.296	2.53	2.114	2.455	0.122	8.22	6.20	10.90
		320 K	0.277	2.50	2.097	2.443	0.120	7.07	6.04	8.28
		330 K	0.211	2.48	2.082	2.435	0.119	6.21	5.87	6.59
5.	T Mix. No 2 (BA+IBMA+BMA) (.3421+.5963+.0616)*	300 K	0.333	2.52	2.127	2.430	0.122	9.49	7.01	12.86
		310 K	0.332	2.49	2.121	2.419	0.121	8.38	6.86	10.23
		320 K	0.261	2.46	2.100	2.407	0.120	7.24	6.33	8.28
		330 K	0.149	2.44	2.084	2.395	0.119	6.63	6.20	6.59
6	T. Mix. No 3 (BA+IBMA+BMA) (.3608+.3144+.3247)*	300 K	0.357	2.54	2.127	2.434	0.125	10.23	7.09	14.78
		310 K	0.334	2.52	2.120	2.430	0.124	9.38	6.97	12.65
		320 K	0.318	2.49	2.103	2.413	0.122	8.69	6.85	11.00
		330 K	0.259	2.47	2.087	2.400	0.119	8.23	6.62	10.25
7	T Mix. No. 4 (BA+IBMA+BMA) (.6910+.0.622+.2488)*	300 K	0.362	2.53	2.128	2.425	0.121	10.36	7.10	15.13
		310 K	0.309	2.50	2.116	2.410	0.119	9.66	7.07	13.18
		320 K	0.297	2.47	2.103	2.396	0.117	8.75	6.96	11.02
		330 K	0.253	2.44	2.089	2.382	0.115	7.75	6.84	8.79

\* Mole fraction of respective components in mixture composition.

### 3. Results and Discussion

The dielectric parameters ( $\epsilon_s$ ,  $\epsilon_\infty$ ,  $\epsilon'$  and  $\epsilon''$ ) and relaxation time ( $\tau_0$ ,  $\tau_1$  and  $\tau_2$ ) of three pure acrylates and their ternary mixture compositions at different temperatures are given in Table 1. It is clear from Table 1 that variation of dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  values of individual components and their ternary mixture compositions has same trend and order of change with temperature which supports our expectation that internal fields of the mixtures are not different from those of pure components. Acrylate molecules under present investigations are non-rigid associative in nature so the molecular interactions among solute components in mixtures cannot be ruled out even in dilute solution of carbon tetrachloride.

Finite value of distribution parameter  $\alpha$  (recorded in Table 1) for pure components and their ternary mixture compositions at different temperatures indicates existence of more than one relaxation process. Degree of distribution of relaxation processes other than molecular relaxation of each component is same as no significant difference in  $\alpha$  - values of molecules are observed. It is also evident from Table 1 that values of distribution parameter  $\alpha$  for all solutes and ternary mixtures decrease with increase in temperature, which shows that at higher temperature molecular rotation of solute molecules become faster and uniform in the solution.

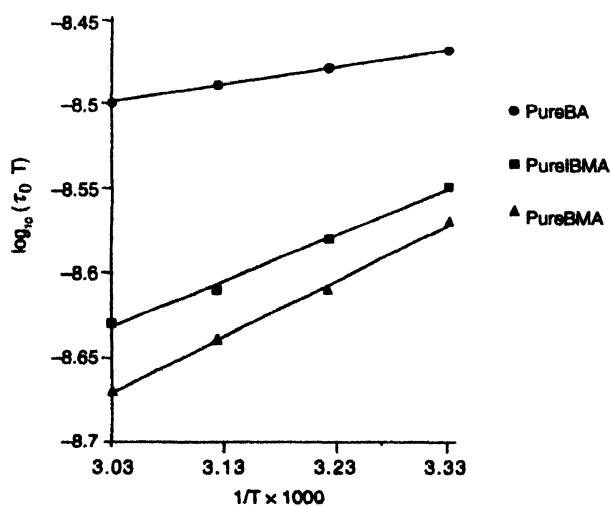
The values of  $\tau_0$ ,  $\tau_1$  and  $\tau_2$  (listed in Table 1) for solutes and their mixtures decrease with increase in temperature. At higher temperature, beside change in molar volume, rate of loss

**Table 2.** Comparison of experimental and computed values of relaxation time using theoretical methods for ternary mixture of acrylates at different temperatures.

Sl. No	Name of the Sample	Temp	Exp. ( $\tau_0$ ) <sub>exp</sub> × 10 <sup>12</sup> , s	Theoretical values of $\tau_0$ calculated by			Percentage deviations		
				Sm Rule	Rm Rule	Y & G Method	SM Rule	RM Rule	Y & G Method
1.	T.Mix. No. 1 (BA + IBMA + BMA)* (.0696+.3035+.6269)	300 K	9.32	9.24	9.21	9.26	0.85	1.18	0.64
		310 K	7.07	8.40	8.35	8.42	-1.92	-1.81	-4.90
		320 K	7.72	7.58	7.52	7.62	1.81	2.59	1.30
		330 K	6.21	6.89	6.81	6.95	-10.95	-9.66	-11.90
2.	T.Mix. No. 2 (BA + IBMA + BMA)* (.3421+.5963+.0616)	300 K	9.49	10.04	9.94	10.09	-5.80	-4.74	-6.32
		310 K	8.38	8.98	8.80	8.83	-7.15	-5.01	-5.36
		320 K	7.24	8.55	8.40	8.63	-15.30	-16.02	-18.78
		330 K	6.63	8.03	7.83	8.14	-21.10	-18.09	-22.70
3.	T.Mix. No. 3 (BA + IBMA + BMA)* (.3608+.3144+.3247)	300 K	10.23	9.97	9.85	10.03	2.54	3.71	1.95
		310 K	9.38	9.10	8.95	9.19	2.98	4.58	2.02
		320 K	8.69	8.45	8.69	8.56	2.76	0.00	1.50
		330 K	8.23	7.90	7.64	8.05	4.00	7.10	7.16
4.	T.Mix. No. 4 (BA + IBMA + BMA)* (.6910+.0622+.2488)	300 K	10.36	10.69	10.52	10.74	-3.18	-1.54	-3.66
		310 K	9.66	10.01	9.82	9.18	-10.66	-1.65	4.90
		320 K	8.75	9.31	9.06	9.40	6.40	3.54	7.40
		330 K	7.75	8.87	8.53	9.00	14.45	10.06	16.12

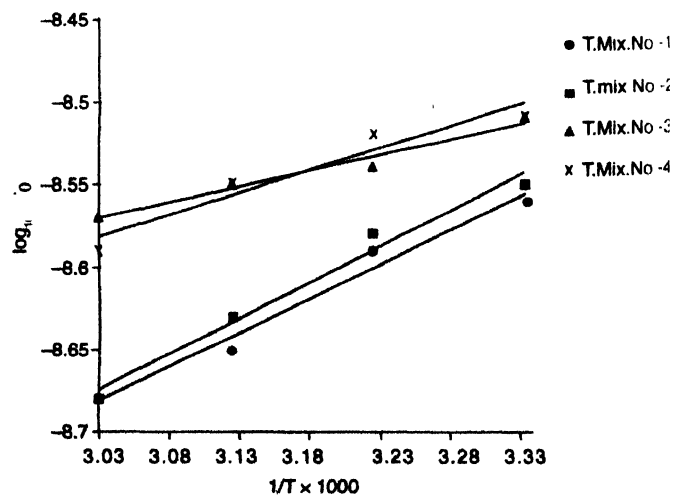
\* Mole fraction of respective components in mixture composition.

of energy due to larger number of collisions dominates and hence molecules reorient with faster rate while field changes its direction. Figures 1 and 2 present variation of  $\log(\tau_0 T)$  v/s  $1/T$  for the three acrylates and their ternary mixtures respectively. These plots show linear relationship within experimental error, which indicates exponential decay of relaxation times with temperature for the dielectric relaxation processes.

**Figure 1.** Plots of  $\log_{10}(\tau_0 T)$  versus  $1/T$  for pure BA, IBMA and BMA in dilute solution of carbon tetrachloride.

For all the solutes and their ternary mixtures, values of  $\tau_2$  are significantly different from  $\tau_0$  and  $\tau_1$ , beyond any

experimental errors. This result confirms the presence of both intermolecular and intramolecular relaxation processes. Higher values of  $\tau_2$  indicate that contribution of intramolecular relaxation is higher in comparison to intermolecular or overall molecular relaxation. Listed  $\tau_0$  values in Table 1 for mixture compositions at four different temperatures lie between  $\tau_1$  values of constituent components. This behavior can be explained in terms of overlapping of two Debye regions and by considering that the degree of overlap changes with change in molar concentration of polar components of the mixture.

**Figure 2.** Plots of  $\log_{10}(\tau_0 T)$  versus  $1/T$  for ternary mixture compositions of BA, IBMA and BMA in dilute solution of carbon tetrachloride.

The experimental values of most probable relaxation time  $\tau_0$  of mixture compositions at four different temperatures are compared with computed  $\tau_0$  values obtained by using eqs. (10-12) and are listed in Table 2. Experimental and computed values are comparable to each other however small deviations may be attributed to experimental uncertainties. At higher temperatures, these deviations are quite large and hence solute-solute and solute-solvent interactions among molecules may dominate relaxation process. An additional term representing interaction among dissimilar molecules of mixture needs to be included in expression of most probable relaxation time  $(\tau_0)_{\text{mix}}$  to improve theoretical basis for the interpretation of relaxation time of mixtures and a variety of mixture compositions at higher temperature range should be taken.

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